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THERMAL CONDUCTIVITIES OF GASEOUS H_2O , D_2O ,
AND THE EQUIMOLAR $H_2O - D_2O$ MIXTURE

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ABSTRACT

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Measurements have been carried out over the temperature range 380-525° K

using a four-cell hot-wire thermal-conductivity apparatus. At the lower temperatures the thermal conductivities of H_2O and D_2O are identical, but at the highest temperature the conductivity of D_2O is larger by 8-9 parts per thousand. Conductivities of the equimolar mixtures lie midway between the conductivities of the pure components. Results are analyzed to test a recent hypothesis that a resonant exchange of rotational quanta causes the thermal conductivity of a polar gas to seem anomalously low in relation to its viscosity. It is concluded that this phenomenon is probably not important in determining the thermal conductivity of water vapor. AUTHOR

INTRODUCTION

Our understanding of heat conduction in polyatomic gases has been considerably enhanced by the recent theoretical studies of Mason and Monchick.¹ Starting with the formal kinetic theory of Wang Chang and Uhlenbeck² and Taxman,³ they have derived explicit expressions for the thermal conductivity of polyatomic gases. By systematically including terms involving inelastic collisions, they derived the modified Eucken expression^{4,5,6} as a first approximation and, as a second approximation, an expression dependent on the relaxation times for the various internal degrees of freedom. Their result may be written

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$$\lambda = \frac{\eta}{M} \left[\frac{5}{2} C_{v_{trans}} + \frac{\rho D_{int}}{\eta} C_{int} - \frac{2}{\pi} \left(\frac{5}{2} - \frac{\rho D_{int}}{\eta} \right)^2 \sum \frac{C_k}{Z_k} \right] \quad (1)$$

Here λ is the thermal conductivity, η is the viscosity, M is the molecular weight, ρ is the density, and D_{int} is the average coefficient for the diffusion of internal energy, while $C_{v_{trans}}$ and C_{int} are the translational and the internal contributions to the molar heat capacity. Z_k is the number of collisions for relaxation of the k^{th} internal mode, while C_k is the heat capacity associated with that mode.

The first two terms in Eq. (1) are simply the modified Eucken approximation, while the third term is important only for small collision numbers. In small, rigid polyatomic molecules these are associated with rotational relaxation. (In flexible molecules vibrational relaxation times may also be small.)

For nonpolar gases D_{int} is commonly assumed to be equal to the self-diffusion coefficient. With this assumption O'Neal and Brokaw^{7,8,9} have analyzed experimental recovery-factor measurements (in essence a direct determination of the quantity $\lambda M / \eta C_v$) so as to obtain collision numbers for rotational relaxation. Since collision numbers for nitrogen, oxygen, carbon dioxide, methane, and hydrogen were found generally in accord with values obtained by other experimental methods, it was concluded that the approximate theory embodied in Eq. (1) is substantially correct. Furthermore, it seems that these collision numbers are determined by the following factors: (1) the molecular mass distribution, (2) the strength of the intermolecular attractive forces, and (3) the molecular asymmetry.

The thermal conductivities of highly polar gases such as hydrogen

fluoride, water, and ammonia appear to be anomalously low in relation to their viscosities. Mason and Monchick¹ suggest that this effect is largely due to a resonant exchange of rotational energy, presumed probable on grazing self-collisions of polar molecules. Hence, a grazing collision with exchange is equivalent to a head-on collision without exchange insofar as the transport of the rotational quantum is concerned. Thus, the diffusion coefficient for internal energy, D_{int} in Eq. (1), is smaller than the self-diffusion coefficient, D_{11} , and is given by the expression

$$D_{int} = \frac{D_{11}}{1 + \delta}, \quad (2)$$

where δ is a correction term calculated from the theory of resonant collisions.

Mason and Monchick¹ give expressions for δ for linear dipoles and also for several types of symmetric tops. The salient factors determining δ are apparent in their result for spherical tops:

$$\delta = \frac{5\pi}{16} \langle a_4 \rangle \left[\frac{3}{16} \frac{\mu h}{\sigma_D kT} \right]^2 \left[\frac{m^{1/2}}{(C_{int}/R) I^{3/2}} \right]. \quad (3)$$

Here $\langle a_4 \rangle$ is the mean value of a dimensionless quantity involving the rotational quantum numbers, taken to be 0.44. Furthermore, μ is the dipole moment, h is Planck's constant, σ_D is the kinetic-theory diameter characteristic of diffusion ($\equiv \sigma [\Omega^{(1,1)*}]^{1/2}$ in the notation of reference 10), k is the Boltzmann constant, m is the molecular mass, R is the universal gas constant, and I is the molecular moment of inertia. (It might be noted that δ for linear dipoles is given by an expression identical to Eq. (3) but for the factor $5\pi/16$.)

As already noted, the collision number is dependent on the molecular mass distribution. This dependence may be characterized as

$$Z_{\text{rot}} \propto \frac{4I}{m\sigma_{\eta}^2} \quad (4)$$

where σ_{η} is viscosity collision diameter $\left(\equiv \sigma \left[\Omega(2,2)^* \right]^{1/2} \right.$ in the notation of reference 10).

It occurred to us that Mason and Monchick's postulate regarding the importance of the resonant exchange of rotational quanta might be tested by measuring the thermal conductivities of deuterated and ordinary polar gases; H_2O and D_2O were chosen because they were readily available.

From Eqs. (1)-(4) it is seen that isotropic substitution of deuterium for ordinary hydrogen will affect the thermal conductivity through increases in molecular weight (10%), internal heat capacity (10-15%), and moments of inertia (80-100%). Thus the moments of inertia are profoundly altered. In the absence of the resonant phenomenon we would expect the thermal conductivity of H_2O to be somewhat larger than that of D_2O . This is a consequence of the smaller mass of ordinary water (see Eq. (1) - viscosities are only proportional to $M^{1/2}$) and also of the smaller moments of inertia which lead to a larger collision number for rotational relaxation (see Eq. (4)). These factors should outweigh the effect of the somewhat greater heat capacity of D_2O .

On the other hand, the resonant correction depends inversely on moment of inertia (Eq. (3)) and, hence, is larger for H_2O . As a consequence, if the resonant exchange of rotational quanta does indeed occur, the conductivities of H_2O and D_2O should be very nearly equal; the conductivity of D_2O may actually be slightly larger.

Mason and Monchick's postulate regarding resonant exchange of rotational energy can be subjected to a further qualitative test. The effect is based on exact resonance; that is, an exact matching of rotational energy levels. Consider now an equimolar mixture of H_2O and D_2O . In such a gas one-half of the collisions are self-collisions of H_2O or D_2O in which resonant exchange of rotational quanta may occur. The remaining collisions are between H_2O and D_2O . In these collisions there is no matching of rotational levels so there should be no resonant exchange. Consequently, we might expect such a mixture to have a thermal conductivity larger than either of the pure constituents. This argument must remain qualitative, however, because we have as yet no analogous theory for mixtures.

The present experiments were initiated to test these theoretical notions regarding the thermal conductivity of polar gases. (A preliminary result using a rather crude apparatus has already been reported.¹¹) Conductivities of H_2O and D_2O were measured at 381.2, 426.1 478.0 and 525.6° K, while the thermal conductivity of the equimolar mixture was measured at the two highest temperatures only. After completion of the present experimentation and data analysis we learned of the recent work of Vargaftik and Zaitseva¹² who have measured the thermal conductivities of H_2O and D_2O from 100-500° C. The present measurements are in qualitative, but not quantitative, agreement with the Russian work.

EXPERIMENTAL

Apparatus and Procedure

The hot-wire thermal-conductivity apparatus has been described in some detail by Coffin and O'Neal¹³. Briefly, it consists of two pairs of

hot-wire cells connected as elements of a constant-current Wheatstone bridge. The voltage unbalance produced when gases of unequal thermal conductivity are introduced into the pairs of cells is measured. The instrument responds to the reciprocal of the thermal conductivity,

$$E - E_{\text{ref}} = b \left(\frac{1}{\lambda} - \frac{1}{\lambda_{\text{ref}}} \right). \quad (5)$$

Here E is the voltage unbalance with a gas of unknown conductivity in one pair of cells and a reference gas in the other pair; E_{ref} is the voltage with the reference gas in both cells. λ and λ_{ref} are the thermal conductivities of the unknown and reference gases, respectively, while b is a constant characteristic of the apparatus (it may be slightly temperature dependent). For this work helium and argon were used as calibrating gases. The conductivities assumed for helium and argon are discussed in the next section.

H_2O and D_2O vapors were supplied to the cells at a pressure slightly above atmospheric from ampules thermostatted in a bath at 104°C (a boiling salt solution). Connecting lines were heated with electrical heating tape to prevent condensation. The gas handling system was in other respects conventional.

In addition to the measurements on ordinary and heavy water vapors, the thermal conductivity of nitrogen was determined at all four temperatures. Also, air, oxygen, and carbon dioxide were measured at 478.0°K . In general, nitrogen served as the reference gas except that D_2O and the equimolar H_2O - D_2O mixture were measured against ordinary water. Thus these small emf's were measured with enhanced precision.

Experimental voltages relative to argon are recorded in Table I. An extra significant figure is given for the isotopic waters to reflect the measured voltage differences among them. The voltages relative to nitrogen were reproducible to about 0.001 mv.

Thermal Conductivities of the Calibrating Gases Helium and Argon

Thermal conductivities for the calibrating gases were assigned after considering experimental viscosity and thermal conductivity data on helium and argon. Because helium and argon are monatomic gases, it is possible to compute conductivity from viscosity through the rigorous theoretical relation¹⁴

$$\lambda = \frac{15}{4} \frac{R}{M} \eta \frac{f_{\lambda}^{(3)}}{f_{\eta}^{(3)}} \quad (6)$$

The functions $f_{\lambda}^{(3)}$ and $f_{\eta}^{(3)}$ are very slowly varying functions of temperature that differ only slightly from unity. Equation (6) is rigorous through the third Chapman-Enskog approximation and has been experimentally verified for helium and argon within a few parts per thousand⁷. The factor $f_{\lambda}^{(3)}/f_{\eta}^{(3)}$ was calculated assuming an exponential-6 force law with appropriate force constants¹⁵; over the temperature range of interest this quotient is greater than unity by 1-3 parts per thousand for argon and 3-4 parts per thousand for helium.

In essence, large scale plots of experimental thermal conductivity were constructed and smooth curves faired through the data¹⁶⁻¹⁹, giving the greatest weight to values computed from recent viscosity measurements, since these data have the highest precision and accuracy.

The conductivities selected for calibration, as well as values at even increments of 100° K are given in Table II. Figures 1 and 2 show the departures of experimental thermal conductivities from the tabulated values for helium and argon, respectively. The data indicated as solid symbols represent actual thermal conductivity measurements, while the open symbols are derived from viscosity measurements and show considerably less scatter.

Experimental Results

The thermal conductivities derived from Tables I and II by means of Eq. (5) are presented in Table III. Again an extra significant figure has been retained for the isotopic waters so as to indicate relationships among them. The values of Table III are generally in accord with previous determinations in the literature. This is illustrated in Fig. 3, where the present data on water vapor and nitrogen are compared with the measurements of Vargaftik and Oleschuk²⁰ and Geib and Schäfer⁽²¹⁾. The agreement is generally satisfactory, although our datum for water at the highest temperature seems to be a bit low.

Also included in Table III are thermal conductivities of H_2O and D_2O interpolated from the recent data of Vargaftik and Zaitseva¹². The agreement in the case of H_2O is entirely satisfactory with deviation from 0.5 to 1.3%. In the case of D_2O , however, there seem to be more serious discrepancies with deviations of as much as 3.5% at the lowest temperature (deviations are systematic rather than random). The apparatus used by Vargaftik and Zaitseva¹² had a single hot-wire thermal-conductivity cell so that H_2O and D_2O were of necessity measured in separate runs. In contrast, in our experiments we have compared H_2O and D_2O directly

against one another. Consequently, we believe our results on D_2O are to be preferred - especially with regard to the values relative to H_2O .

ANALYSIS AND DISCUSSION

The experimental data on the pure gases were analyzed as follows: Eq. (1) was assumed correct and used to calculate the collision number Z_{rot} and resonant correction δ required to reproduce the experimental data. Although we have made no assumption as to the absolute magnitudes of these parameters, we have assumed that the relative magnitudes may be calculated from theoretical expressions in terms of molecular masses, moments of inertia, dipole moments, etc. of the two molecules (values used are shown in Table IV).

Certain temperature-dependent quantities that are needed, such as viscosity and heat capacity, are shown in Table V. Viscosities of heavy water were computed assuming the viscosity collision cross section of D_2O is 3% larger than that of H_2O . This was deduced from the viscosity measurements of Bonilla, Wang, and Weiner¹⁸ and is qualitatively in accord with the somewhat higher dipole moment of D_2O .

As was mentioned in the introduction, Mason and Monchick¹ developed expressions for the resonant correction for linear dipoles and symmetric tops. They suggest that slightly asymmetric tops can be treated in the following manner. If I_A is the moment of inertia about the dipole axis (in this case, the figure axis of the molecule) and I_B and I_C are the other two moments, one uses the symmetric top formulas replacing I_B by $(I_B I_C)^{1/2}$.

From Table IV it is clear that H_2O and D_2O are in fact highly asymmetric tops (I_B and I_C differ by a factor of three). In the absence of any better procedure, we assume that H_2O and D_2O can be treated as slightly asymmetric tops and find that they must then be classified as near-spherical tops. For such molecules the resonant correction is

$$\delta = \frac{5\pi}{16} \langle a_4 \rangle \left(\frac{3}{16} \frac{\mu k}{\sigma_D kT} \right)^2 \frac{R}{C_{int}} \frac{m^{1/2}}{I_A (I_B I_C)^{1/4}} \left[\frac{5}{4} - \frac{(I_B I_C)^{1/2}}{4 I_A} \right]^{-\frac{7}{2}}. \quad (7)$$

(Note that Eq. (7) reduces to Eq. (3) if the moments of inertia are equal.) From Eq. (7) and Table IV (and assuming the diffusion collision cross section for D_2O is also 3% larger than for H_2O) we find

$$\delta_{D_2O} / \delta_{H_2O} = 0.3613 C_{int_{H_2O}} / C_{int_{D_2O}}. \quad (8)$$

Eqs. (1) and (4) suggest a simple average moment of inertia may be used to calculate a mean Z_{rot}^{-1} . Hence we have assumed

$$Z_{D_2O} / Z_{H_2O} = 0.5933. \quad (9)$$

Finally, the dimensionless quantity $\rho D_{11} / \eta$ involving the self-diffusion coefficient was computed as $(6/5) \langle A^* \rangle^{22}$. The quantity $\langle A^* \rangle$ is a ratio of collision integrals (essentially the ratio of the viscosity and diffusion cross sections) and is quite insensitive to temperature and the details of the intermolecular force law, at least for spherically symmetric potentials. In the absence of experimental information on self-diffusion in water vapor, we have taken $\langle A^* \rangle$ from calculations for a modified (angle independent) Stockmeyer potential²³. This is the only place in the analysis where we have had to make any assumption about the intermolecular force law.

Collision numbers for rotational relaxation and resonant corrections deduced from the data analysis are presented in Table V. The collision numbers for H_2O (One to three collisions) seem low for a molecule with such small moments of inertia. (Methane, for example, requires perhaps 10-15 collisions^{8,9}.) However, these low values can perhaps be rationalized by noting that the large dipole moment causes a large deviation from spherical symmetry in the intermolecular force field and consequently promotes energy transfer between rotation and translation.

The resonant corrections are seen to be somewhat smaller than values computed from Eq. (7), especially at the lower temperatures. The derivation of Eq. (7) involves among other approximations the replacement of summations by integrations. In the case of ammonia, Monchick and Mason¹ carried out the direct summation and found that the analytic expression for the resonant correction gave too high a value at low temperature. A similar deviation for water might have been anticipated. All in all, the data on pure H_2O and D_2O tend to confirm Mason and Monchick's postulate regarding the importance of resonant transfer of rotational quanta in reducing the heat conductivity of highly polar gases.

Unfortunately, the data on the H_2O - D_2O mixtures seem to negate this conclusion. It is a simple matter to compute the thermal conductivities of H_2O and D_2O using the collision numbers of Table V but omitting the resonant correction (values so computed are shown in Table VI). The effect of the resonant correction is substantial since it reduces the calculated conductivity of D_2O by 10% and H_2O by almost 20%.

In H_2O - D_2O mixtures the collisions between H_2O and D_2O molecules should not involve resonant exchange and should consequently be

characterized by these nonresonant conductivities. Although we have no rigorous mixture theory for polyatomic gases, we may make a reasonable prediction based on monatomic gas theory. The rigorous expression²⁴ for a binary mixture of isotopic monatomic gases of nearly equal mass is, to a very good approximation,

$$\frac{1}{\lambda_{\text{mix}}} = \frac{x_1^2}{\lambda_1} + \frac{2x_1x_2}{\lambda_{12}} + \frac{x_2^2}{\lambda_2}. \quad (10)$$

Here x_1 and x_2 are the mole fractions of the component gases, while λ_1 and λ_2 are their thermal conductivities. The quantity λ_{12} is defined by Eq. (8.2-34) of Reference 10. For isotopic species the equation reduces to

$$\lambda_{12} = \left[\frac{1}{2} (\lambda_1^2 + \lambda_2^2) \right]^{1/2}. \quad (11)$$

Clearly, the first and third terms of Eq. (10) correspond to self collisions, whereas the second term arises from collisions between the unlike species. Thus it would seem a reasonable approach to compute λ_{12} from Eq. (11) using the nonresonant conductivities of Table VI. Thermal conductivities of the equimolar mixtures can then be obtained from Eq. (10) using the measured values for H_2O and D_2O . Results in Table VI show the computed mixture conductivities exceed the experimental values by about 8%. This is far beyond the range of any conceivable experimental uncertainty. As a matter of fact, the experimental mixture conductivities fall almost exactly midway between the conductivities of the pure components.

In our opinion, this suggests rather strongly that a resonant ~~ex~~ change of rotational quanta does not play an important role in determining the thermal conductivity of water vapor. Admittedly Eq. (10) is not rigorous for mixtures of polyatomic gases (a correct formulation would be considerably more complicated and involve, among other things, relaxation times among the like and unlike molecules explicitly). Nonetheless, we feel that Eq. (10) must be a good approximation for mixtures of isotopically substituted polyatomic gases because of its simple collisional interpretation. In computing λ_{12} from fictitious nonresonant conductivities of the pure gases, we are tacitly assuming that the collision number for D_2O relaxing H_2O is the same as for the self-relaxation of H_2O (with a similar assumption for H_2O relaxing D_2O). This is probably not strictly correct, but if Eq. (4) is any guide, the assumption is in error by no more than 10% (due to the mass difference - more likely 5%, since an average mass is probably appropriate). It would seem to us to be a most remarkable coincidence indeed if the collision numbers for the unlike interactions were smaller than those for self-collisions so as to exactly compensate for absence of resonant exchange of rotational quanta in $H_2O - D_2O$ collisions.

CONCLUDING REMARKS

Although the experimental conductivities of pure H_2O and D_2O are consistent with the postulate¹ that a resonant exchange of rotational quanta is important in determining the thermal conductivity of polar gases, the data on the equimolar H_2O-D_2O mixture seem to refute this idea. Nonetheless, the fact that the conductivity of water vapor appears anomalously low in relation to its viscosity needs an explanation. Tentatively,

we suggest that exchange of rotational energy on grazing collisions is indeed important, but it is essentially classical rather than quantum mechanical. Since a large dipole moment causes a long range asymmetry in the intermolecular force field, it should promote such exchange. However, if the phenomenon is classical, exact matching of rotational energy levels is not a requirement, and exchange between dissimilar polar molecules should occur.

These conclusions are not definitive because of two theoretical shortcomings: we do not as yet have adequate theories for asymmetric top molecules or polar gas mixtures. The first shortcoming is overcome most easily by studying gas pairs for which the theory does exist - linear dipoles, such as HCl and DCl, and symmetric tops, such as NH₃ and ND₃. We hope to initiate such experiments shortly. In the meantime, perhaps a theory for gas mixtures will be forthcoming.

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TABLE I. Experimental emf measurements relative to argon (mv).

Gas	Temperature, °K			
	381.2	426.1	478.0	525.6
He	5.030	5.167	5.186	5.208
N ₂	1.730	1.800	1.791	1.802
D ₂ O	0.806 ₀	1.126 ₅	1.413 ₃	1.640 ₈
H ₂ O	0.808 ₄	1.128 ₅	1.386 ₀	1.604 ₄
0.5 H ₂ O - 0.5 D ₂ O			1.400 ₀	1.626 ₄
O ₂			2.091	
CO ₂			0.980	
Air			1.861	

TABLE II. Thermal conductivities of helium and
argon assumed for calibration purposes
(microcalories $\text{cm}^{-1} \text{sec}^{-1} \text{ }^{\circ}\text{K}^{-1}$).

Temperature, $^{\circ}\text{K}$	Helium	Argon
300	370.9	42.42
381.2	437.4	51.26
400	452.3	53.27
426.1	472.8	55.82
478.0	512.8	60.79
500	529.5	62.85
525.6	548.6	65.12
600	603.4	71.51

TABLE III. Experimental thermal conductivities
(microcalories $\text{cm}^{-1} \text{sec}^{-1} \text{ } ^\circ\text{K}^{-1}$).

Gas	Temperature, $^\circ\text{K}$			
	381.2	426.1	478.0	525.6
D_2O	59.7 ₂	69.1 ₁	80.0 ₁	90.1 ₅
H_2O	59.7 ₄	69.1 ₄	79.5 ₂	89.3 ₉
0.5 H_2O - 0.5 D_2O			79.7 ₇	89.8 ₅
N_2	73.6	80.6	87.4	93.7
O_2			94.3	
CO_2			72.9	
Air			88.9	
^a D_2O	57.6	66.8	78.8	90.6
^a H_2O	59.2	68.2	79.1	90.0
^a Reference 12.				

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TABLE IV. Molecular properties of H₂O and D₂O.

	H ₂ O	D ₂ O
^a Moments of Inertia, gm cm ² ×10 ⁴⁰	1.0224 ^b 1.9180 2.9404	1.833 ^b 3.841 5.674
Molecular weight	18.0160	20.029
^c Dipole moment, esu-cm×10 ¹⁸	1.844	1.861

^aA. S. Friedman and L. Haar, J. Chem. Phys. 22,
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^bFigure axis.

^cL. G. Groves and S. Sugden, J. Chem. Soc. 1935,
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TABLE V. Data analysis for pure H₂O and D₂O.

		Temperature, °K			
		381.2	426.1	478.0	525.6
Viscosity of H ₂ O, μpoise		^a 127.4	^b 143.2	^b 164.0	^b 184.9
^c (C _{int} /R)	H ₂ O	1.60069	1.64771	1.70781	1.76743
	D ₂ O	1.75277	1.83355	1.93036	2.02233
^d ρ _{D₁₁} /η (= $\frac{6}{5} \langle A^* \rangle$)		1.316	1.320	1.325	1.327
Z _{rot}	H ₂ O	2.7	2.5	2.3	2.0
	D ₂ O	1.6	1.5	1.3 ₅	1.2
δ _{H₂O}	expt.	.48	.40	.38	.36
	calc.	.64	.53	.44	.38
δ _{D₂O}	expt.	.16	.13	.12	.11
	calc.	.21	.17	.14	.12

^aJ. Hilsenrath et al, Tables of Thermal Properties of Gases, National Bureau of Standards Circular 564 (1955).

^bJ. Kestin and H. E. Wang, Physica 26, 575 (1960).

^cSee Footnote a, Table IV.

^dReference 23.

TABLE VI. Thermal conductivities for analysis
of the data on H₂O-D₂O mixtures
(microcalories cm⁻¹ sec⁻¹ K⁻¹).

Gas	Temperature, °K	
	478.0	525.6
H ₂ O, (expt.)	79.5	89.4
H ₂ O, nonresonant (calc.)	98.3	111.1
D ₂ O, (expt.)	80.0	90.2
D ₂ O, nonresonant (calc.)	88.8	100.3
λ ₁₂ , nonresonant (calc., Eq. (11))	93.7	105.8
Equimolar H ₂ O-D ₂ O (calc., Eq. (10))	86.2	97.1
Equimolar H ₂ O-D ₂ O (expt.)	79.8	89.9

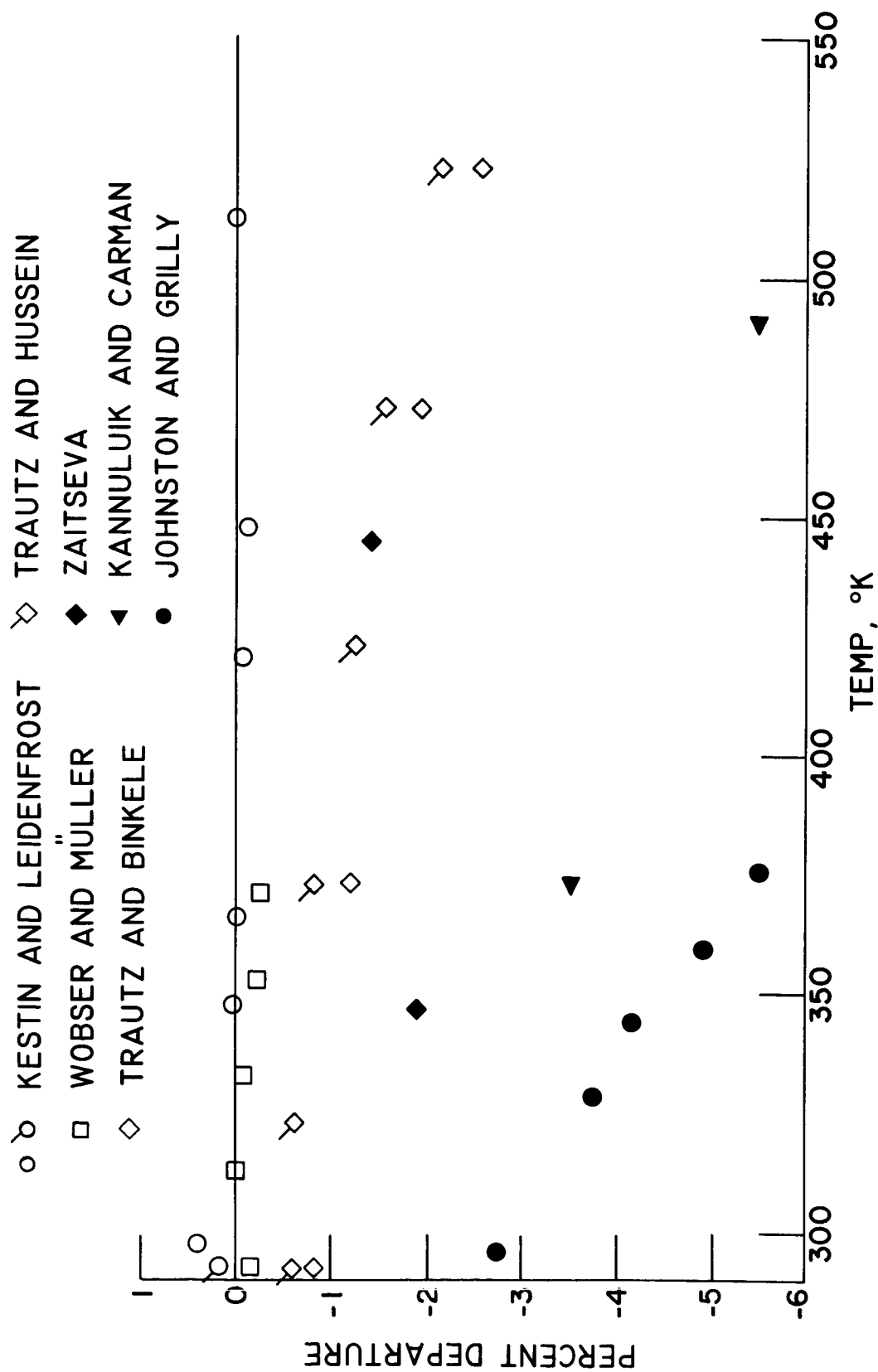


Fig. 1. - Departure of experimental thermal conductivities from tabulated values for helium.
(Solid symbols are conductivity measurements; open symbols calculated from viscosity data.)

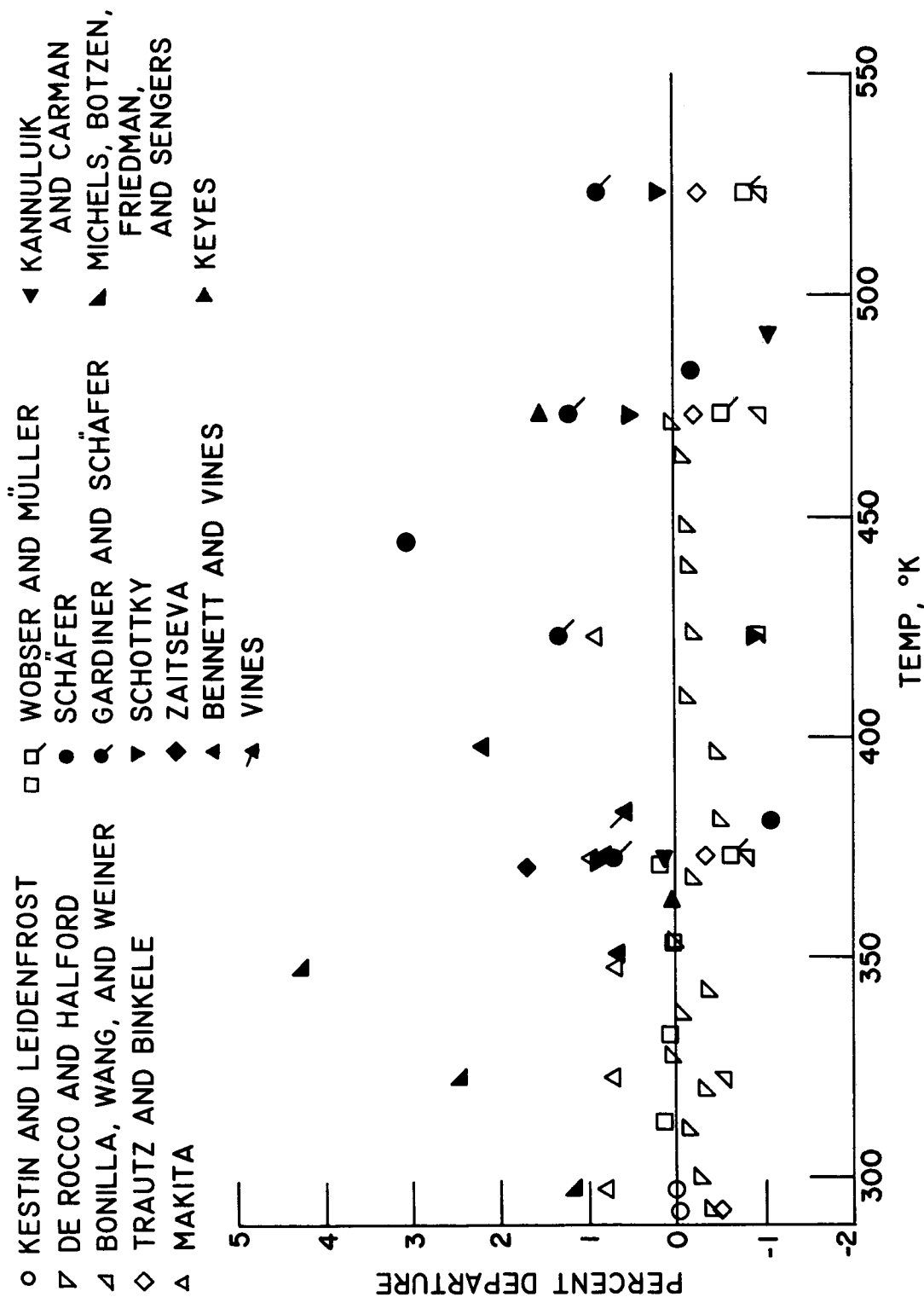


Fig. 2. - Departure of experimental thermal conductivities from tabulated values for argon.
 (Solid symbols are conductivity measurements; open symbols calculated from viscosity data.)

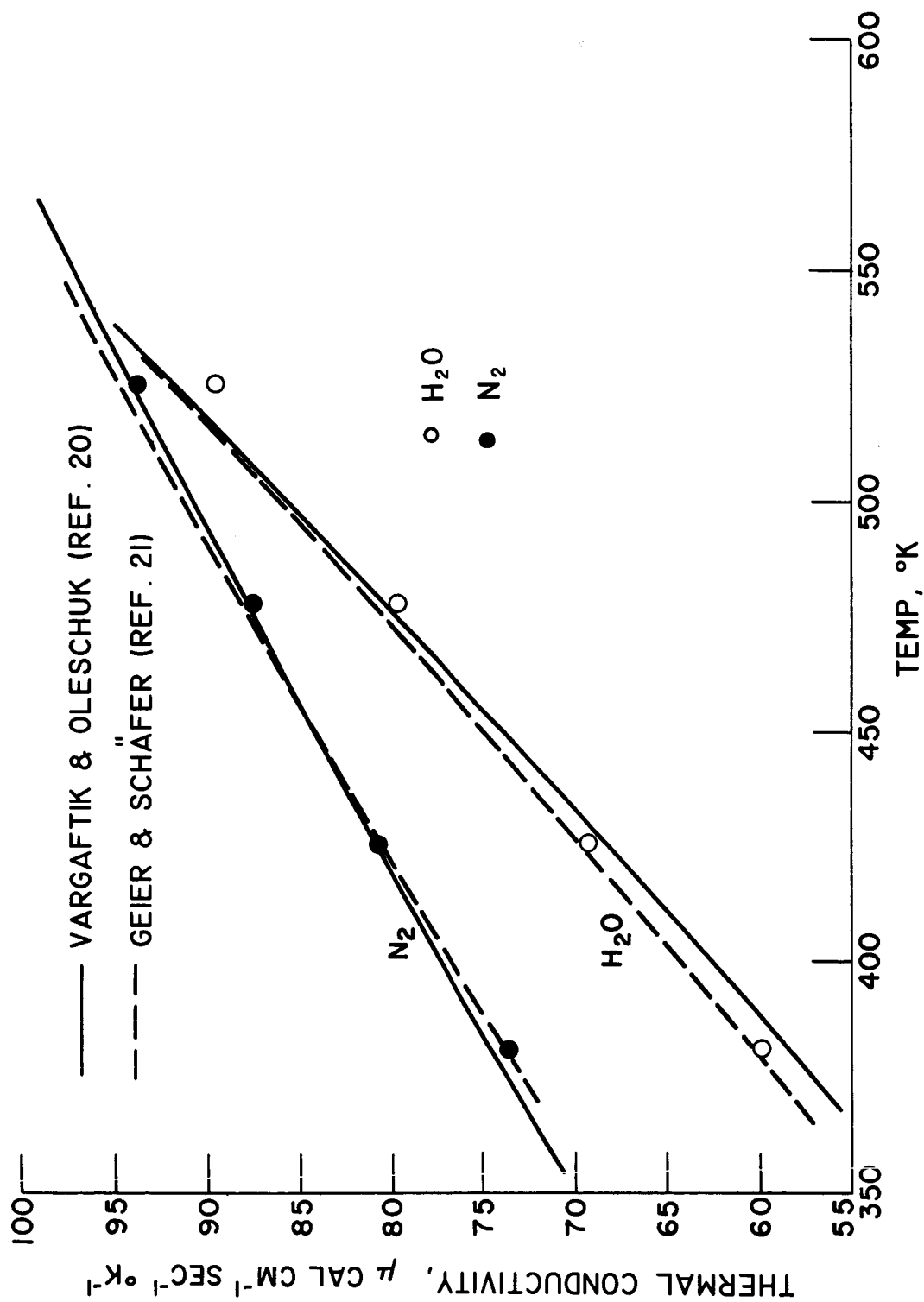


Fig. 3. - Comparison of nitrogen and water thermal conductivities with literature values.